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DRY CLEANING DETERGENT COMPOSITION

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[There are no amendments to this patent.]

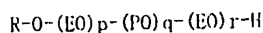
## Abstract

### Task

To obtain a dry cleaning detergent composition appropriate for dry cleaning using a petroleum solvent as a washing medium.

### Solving means

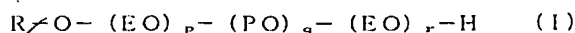
A dry cleaning detergent composition containing 20-60 wt% of at least one nonionic surfactants represented by the following general formula:



(where R is a C<sub>8-18</sub> alkyl group or alkenyl group, EO is an oxyethylene group, PO is an oxypropylene group, p, q, and r are average number of moles added and represent figures that satisfy the relations of  $p > 0$ ,  $r > 0$  and  $q = 1-4$ ,  $p + q + r = 6-16$ , and  $p + r = 5-14$ ). Since the washing performance, recontamination preventing capability, and hydrating performance are excellent, it is appropriate for dry cleaning using a petroleum solvent.

## Claims

1. A dry cleaning detergent composition characterized by the fact that it contains 20-60 wt% of at least one nonionic surfactants represented by the following general formula (I):



(where R is a C<sub>8-18</sub> alkyl group or alkenyl group, EO is an oxyethylene group, PO is an oxypropylene group, p, q, and r are average numbers of moles added and represent figures that satisfy the relations of  $p > 0$ ,  $r > 0$  and  $q = 1-4$ ,  $p + q + r = 6-16$  and  $p + r = 5-14$ ).

2. The dry cleaning detergent composition described in Claim 1, in which it further contains 10-40 wt% of an anionic surfactant.

3. The dry cleaning detergent composition described in Claim 1 or 2, in which it further contains 5-30 wt% of a cationic surfactant.

4. The dry cleaning detergent composition described in Claim 1, 2, or 3, in which it further contains a nonionic surfactant other than the nonionic surfactant represented by the general formula (I), and the total content of the nonionic surfactants in the composition is 20-60 wt%.

### Detailed explanation of the invention

[0001]

#### Technical field of the invention

The present invention relates to a dry cleaning detergent composition appropriate for dry cleaning using a petroleum solvent as a washing medium.

[0002]

#### Prior art and problems to be solved by the invention

Dry cleaning is a washing method using an organic solvent instead of water as a washing medium. As such organic solvents, tetrachloroethylene, trichloroethane, trichlorotrifluoroethane and other halogenated hydrocarbon solvents, petroleum solvents consisting of mixtures of paraffin hydrocarbons, naphthene hydrocarbons, aromatic hydrocarbons, and so on are used.

[0003]

However, from the aspects of adverse effects on the environment and safety recently, the usage of halogenated hydrocarbon solvents has been regulated. In the 4<sup>th</sup> Montreal Protocol Signatory Nations Conference in November 1992, it was decided that the manufacture of trichloroethane and trichlorotrifluoroethane was completely abolished at the end of 1995 (Tokushi Takeda, Fine Chemicals 24, (No. 12) 13 (1995)). Therefore, it has been anticipated to proceed the shifting of dry cleaning that uses petroleum solvents instead of these halogenated hydrocarbon solvents.

[0004]

In dry cleaning, together with organic solvents to remove oil-soluble dirt, dry cleaning detergents obtained by blending of a variety of surfactants for the removal of water-soluble dirt or solid dirt are generally used in combination. In dry cleaning using petroleum solvents, a treating liquid called sasara [transliteration] liquid is used in the pretreatment. The sasara liquid is a material used to remove water-soluble dirt or stains, that come off difficultly by washing, with a sprayer or a brushing treatment prior to washing with a dry cleaning machine. As a common recipe, a material consisting of a petroleum solvent/a dry cleaning detergent/water = 8/1/1 (volumetric ratios) has been adopted.

[0005]

As performances required for the dry cleaning detergent, the washing performance, the recontamination preventing capability, the hydrating performance (the water-solubilizing capability), the electrostatic preventing capability, the softening performance and so on can be

mentioned. In order to have a homogeneous, stable material for a washing medium system containing the previously mentioned sasara liquid in dry cleaning, it is especially important that the hydrating performance of the dry cleaning detergent is high.

[0006]

However, in the case of using a petroleum solvent in a conventional dry cleaning detergent, there has been no material that satisfies the hydrating performance as well as the washing performance, recontamination-preventing capability, etc. Such an important is desired.

[0007]

Thus, the present invention has an objective to provide a dry cleaning detergent composition that also corresponds to a change in the washing medium in dry cleaning, is especially appropriate in the case using a petroleum solvent as a washing medium, and also satisfies the hydrating performance together with the washing performance and the recontamination preventing capability.

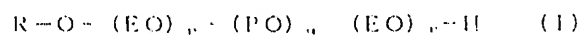
[0008]

Means to solve the problems

As a result of zealous investigations, the present inventors have discovered that the hydrating performance can be improved without decreasing the washing performance, the recontamination preventing performance or the like by containing a nonionic surfactant obtained by the addition of ethylene oxide and propylene oxide in a specific sequence and ratio into a specific alcohol, instead of a conventional polyoxyethylene nonionic surfactant. The present invention has been accomplished.

[0009]

In other words, the present invention provides a dry cleaning detergent composition characterized by the fact that it contains 20-60 wt% of at least one nonionic surfactant represented by the following general formula (I):



(where R is a C<sub>8-18</sub> alkyl group or alkenyl group, EO is an oxyethylene group, PO is an oxypropylene group, p, q, and r are average numbers of moles added and represent figures that satisfy the relations of p > 0, r > 0 and q = 1-4, p + q + r = 6-16 and p + r = 5-14).

[0010]

Implementation embodiments of the invention

In the general formula (I), R represents a C<sub>8-18</sub> alkyl group or alkenyl group. Among these, alkyl groups derived from linear or branched primary saturated alcohols or linear secondary saturated alcohols are preferred. Furthermore, in the general formula (I), the addition sequence and ratio of ethylene oxide and propylene oxide for the introduction of the oxyethylene group and the oxypropylene group are to be restricted to the representation and the definition of the general formula (I). The cases other than this are outside the scope of the present invention.

[0011]

The nonionic surfactant of the general formula (I) can be obtained by a method in which ethylene oxide is added into a higher alcohol, then propylene oxide is added, and ethylene oxide is subjected to block addition. As the catalysts for use in this addition reaction, in addition to basic catalysts and acid catalysts, MgO-ZnO, MgO-SnO, MgO-TiO<sub>2</sub> and MgO-SbO described in Japanese Kokai Patent Application No. Hei 7[1995]-227540, the same Mg catalysts described in Japanese Kokai Patent Application No. Hei 1[1989]-164437, and other catalysts rendering a narrow alkylene oxide distribution can be used. Among these catalysts, basic catalysts are preferred from the cost aspect. In particular, potassium hydroxide is preferred.

[0012]

Next, the method for the manufacture of the nonionic surfactant of the general formula (I) for the case of using potassium hydroxide will be explained. First of all, in a C<sub>8-18</sub> saturated or unsaturated higher alcohol, potassium hydroxide is charged. After nitrogen substitution, it is dehydrated by keeping it at 100-110°C and 10-50 torr for 30 min to 1 h. Next, the addition of ethylene oxide under the conditions of 100-170°C and 3-6 kg/cm<sup>2</sup>, and the addition of ethylene oxide under the conditions of 100-170°C and 3-6 kg/cm<sup>2</sup> are carried out in sequence. Afterwards, by neutralization with an acid agent (acetic acid, lactic acid, glycolic acid or the like) at an equimolar amount as the potassium hydroxide added, a nonionic surfactant of the general formula (I) is obtained. The amounts of usage of ethylene oxide and propylene oxide are determined according to the number of moles of the higher alcohol used as a feedstock so that the conditions defined in the general formula (I) are satisfied.

[0013]

The content of the nonionic surfactant represented by the general formula (I) in the dry cleaning detergent composition is 20-60 wt%, preferably 30-50 wt%, for rendering sufficient detergent and hydrating performance, together with the consideration of economy.

[0014]

With an objective to improve detergency, an anionic surfactant may be further blended in the dry cleaning detergent composition of the present invention. There are no special restrictions on the anionic surfactants as long as they are generally used as detergent components. For example, sulfosuccinic acid dialkyl esters or their salts, polyoxyethylene alkyl ether phosphoric acid esters or their salts, polyoxyethylene alkyl ether sulfuric acid esters or their salts, and higher fatty acids or their salts can be mentioned. The amount of blending of the anionic surfactants in the dry cleaning detergent composition is preferably 10-40 wt%. In particular, 10-30 wt% is preferred.

[0015]

With an objective to render an electrostatic prevention performance and a softening performance, a cationic surfactant may be further blended into the dry cleaning detergent composition of the present invention. There are no special restrictions on the cationic surfactants as long as they are generally used as detergent components. For example, alkyl dimethyl hydroxyethyl ammonium-para-toluene sulfonic acid salts, alkyl dimethyl hydroxyethyl ammonium glycolic acid salts, and alkyl dimethyl ethyl ammonium monoethyl sulfuric acid salts can be mentioned. The amount of blending of the cationic surfactants in the dry cleaning detergent composition is preferably 5-30 wt%. In particular, 5-20 wt% is preferred.

[0016]

With an objective to improve detergency and recontamination-preventing capability, a nonionic surfactant other than that of the general formula (I) may be further blended into the dry cleaning detergent composition of the present invention. There are no special restrictions on these nonionic surfactants as long as they are generally used as detergent components. For example, higher fatty acid alkanolamides or their ethylene oxide adducts, and sorbitan fatty acid esters can be mentioned. This nonionic surfactant other than that of the general formula (I) is blended into the dry cleaning detergent composition so that the total content of the nonionic surfactants also including the nonionic surfactant of the general formula (I) is 20-60 wt%, preferably 30-50 wt%.

[0017]

In the dry cleaning detergent composition of the present invention, in addition to the surfactants mentioned previously, a dry cleaning solvent may be blended as a balancing agent. There are no special restrictions on these solvents. Petroleum solvents containing paraffin hydrocarbons (boiling points 120-220°C), naphthene hydrocarbons or aromatic hydrocarbons,

and so on can be mentioned. In addition, water, a viscosity reducing agent, a corrosion inhibitor, an antibacterial agent, and so on may also be blended.

[0018]

For the consideration of rust-preventing characteristics, it is preferable that the pH for the dry cleaning detergent composition of the present invention is adjusted to a range of 6.0-8.0. As a pH-adjusting agent, an alkanolamine is preferred from the aspects of dissolution characteristics and storage stability.

[0019]

The dry cleaning detergent composition of the present invention is generally used after dilution so that its content is 0.1-5 vol% with respect to a dry cleaning solvent.

[0020]

Application examples

The present invention will be further explained in detail with application examples in the following. However, the present invention is not to be restricted to these.

[0021]

#### Production Examples 1-4

The nonionic surfactants 1-4 represented by the general formula (I) for use in the application examples were manufactured according to the following method by the adjustment of the amounts of addition according to the numbers of moles of ethylene oxide and propylene oxide added.

[0022]

In a 5-L rotary stirred autoclave provided with two measuring tanks for ethylene oxide use and propylene oxide use, 500 g lauryl alcohol (commercial product name Kalcohol 2098, manufactured by Kao Co., Ltd.) and 3.0 g potassium hydroxide were charged. Afterwards, after substitution of the inside of the autoclave with nitrogen, it was heated to 110°C. It was dewatered by heating to 110°C and maintaining it at 40 torr for 1 h. Next, it was heated to 150°C. Ethylene oxide was introduced into the autoclave at an amount (an amount equivalent to p in the general formula (I)) corresponding to the desired nonionic surfactant, under a pressure of 3.5 kg/cm<sup>2</sup>. Afterwards, it was cooled to 120°C. Propylene oxide was introduced into the autoclave at an amount (an amount equivalent to q in the general formula (I)) corresponding to the desired nonionic surfactant, under a pressure of 3.5 kg/cm<sup>2</sup>. The reaction was carried out until the



pressure was decreased to a constant level. Afterwards, it was heated again to 150°C. Ethylene oxide was introduced into the autoclave at an amount (an amount equivalent to  $r$  in the general formula (I)) corresponding to the desired nonionic surfactant, under a pressure of 3.5 kg/cm<sup>2</sup>. The reaction was carried out until the pressure was decreased to a constant level. It was neutralized with 3.5 g acetic acid, and a nonionic surfactant of the general formula (I) was obtained.

[0023]

Application Examples 1-7 and Comparative Examples 1-5

The dry cleaning detergent compositions with compositions shown in Tables 1 and 2 for application examples and comparative examples were manufactured. The washing performance, the recontamination-preventing capability, and the hydrating performance were tested. The details of the components in Tables 1 and 2 are given in the following. The numerical values are expressed in wt%. The results are shown in Tables 1 and 2.

[0024]

\* 1: In general formula (I),  $R = n-C_{12}H_{25}$ ,  $p = 2.5$ ,  $q = 1.5$ ,  $r = 3$

\* 2: In the general formula (I),  $R = n-C_{12}H_{25}$ ,  $p = 5$ ,  $q = 1.5$ ,  $r = 5$

\* 3: In the general formula (I),  $R = n-C_{12}H_{25}$ ,  $p = 7$ ,  $q = 1.5$ ,  $r = 7$

\* 4: In the general formula (I),  $R = n-C_{12}H_{25}$ ,  $p = 5$ ,  $q = 4$ ,  $r = 5$

\* 5: Ethylene oxide 3 mol adduct

\* 6: Manufactured by Nippon Catalyst Co., Ltd. commercial product name Softanol

[transliteration] 50. Ethylene oxide 5 mol adduct of C<sub>12</sub>-C<sub>14</sub> secondary alcohols

\* 7: Manufactured by Nippon Petroleum Co., Ltd. commercial product name Naphtezol

[transliteration] L.

[0025]

Test Example 1 (washing performance test)

(1) Preparation of test cloth

10 x 10 cm wool was uniformly coated with 2 g of the model sebum dirt described in the following. Sebum dirt contaminated cloth (artificially contaminated cloth) as test cloth was obtained.

(Model sebum dirt)

Cotton seed oil                      60 wt%

Cholesterol                          10 wt%

Oleic acid	10 wt%
Palmitic acid	8 wt%
Solid and liquid paraffins	10 wt%
Asahi carbon black	2 wt%

[0026]

#### (2) Test method

The artificially contaminated cloth was cut into a 6 x 6 cm cloth piece and used as the test cloth. Four sheets of this test cloth were used as one set. These were placed in a 200-mL separatory funnel. These were washed with the material placed in a shaking machine (manufactured by Taiyo Scientific Ind. Co., Ltd., Taiyo Recipro Shaker SR-II) under the following conditions. They were then dried at ambient temperature. The reflectivities at 550 nm for the raw cloth and the test cloth before and after washing were measured with an autorecording color meter (manufactured by Shimazu Mfg. Co.,). The washing ratio was calculated by the following equation. The measured average value of four sheets was evaluated as the washing performance.

Washing ratio (%) =  $\frac{L_0 - L_2}{L_0 - L_1} \times 100$

$L_0$ : Reflectivity of the raw cloth

$L_1$ : Reflectivity of the test cloth before washing

$L_2$ : Reflectivity of the test cloth after washing

[0027]

#### (3) Washing conditions

Dry cleaning petroleum type solvent: Exxon D-40 (100 mL, manufactured by Exxon Chemical Co.)

Dry cleaning detergent composition: 1.0 vol %.

Temperature: 20°C

Shaking time: 10 min

[0028]

#### Test Example 2 (Recontamination preventing capability test)

Raw cloth (wool) was cut into 6 x 6 cm pieces for use as test cloth. Four sheets of this test cloth were used as one set. As a seed of dirt for recontamination, one sheet of the artificially contaminated cloth (wool, 6 x 6 cm) described previously was added. This was placed in a

200-mL separatory funnel. These were washed with a material placed in the shaking machine (manufactured by Taiyo Scientific Ind. Co., Taiyo Recipro Shaker SR-II), under the same conditions as in Test Example 1. They were dried at ambient temperature. Reflectivities at 550 nm for the raw cloth and the test cloth (raw cloth) after washing were measured with an auto-recording color meter (manufactured by Shimazu Mfg. Co.). The recontamination ratio was calculated with the following equation. The measured average value of the four sheets was evaluated as the recontamination-preventing capability.

Recontamination ratio (%) = //insert F p.4//

$L_0$ : Reflectivity of the raw cloth

$L_2$ : Reflectivity of the test cloth (raw cloth) after washing

[0029]

Test Example 3 (Hydrating performance test)

(1) State during mixing

A material with ratios of Exxon D-40/a dry cleaning detergent composition/ion-exchange water = 8 mL/1 mL/1 mL was placed in a test tube. The state after good mixing was observed by visual inspection. Since the transparency even during mixing is a condition for ease in preparation of the sasara liquid, with the consideration of this point, it was judged according to the following criteria.

○: Transparent during mixing

△: Translucent during mixing

X: Opaque during mixing

[0030]

(2) Water solubilization amount

In a 200-mL emulsification test tube, 100 mL Exxon D-40 and 1 mL of a dry cleaning detergent composition were placed and stirred. While a small amount of ion-exchange water was being added into this by using a microcylinder each time, it was stirred vigorously. After stirring, it was allowed to stand and observed by visual inspection. The amount of the ion-exchange water causing a white turbidity of the solution was the maximum solubilization amount (mL).

[0031]

Table 1

		(1) 実 施 例						
		1	2	3	4	5	6	7
(3) ドライクリーニング用洗浄剤組成物	(3) ③ 非イオン界面活性剤1 <sup>*1</sup>	43				33		
	非イオン界面活性剤2 <sup>*2</sup>		36				36	
	非イオン界面活性剤3 <sup>*3</sup>			38				38
	非イオン界面活性剤4 <sup>*4</sup>				30			
	ポリオキシエチレンニルフェニルエーテル <sup>*5</sup>							
	ポリオキシエチレンアルキルエーテル <sup>*6</sup>							
	ラウリン酸ジエタノールアミド					10		
	ソルビタンモノラウレート				10			
	スルホコハク酸ジ-2-エチルヘキシルエステルNa			12	8	8		
	ポリオキシエチレンラウリルエーテルセスキリン酸エステル <sup>*5</sup>				10	10		
	ステアarylジメチルヒドロキシエチルアンモニウム-パラトルエンスルホン酸塩							12
	ステアarylジメチルヒドロキシエチルアンモニウム-グリコール酸塩		8				8	
	ステアarylジメチルエチルアンモニウム-モノエチル硫酸塩	7						
	トリエタノールアミン				3	3		
	水			2	2	2		2
	石油系溶剤 <sup>*7</sup>	50	56	48	37	34	56	48
	pH(原液, 25°C)	7.4	7.5	6.8	7.0	7.0	6.5	7.5
(4) 評価結果	(4) ④ 洗浄率(%)	62	60	68	65	67	61	64
	再汚染率(%)	8	7	9	9	8	8	9
	抱水性能	○	○	○	○	○	○	○
	(混合時の状態) (6) (水可溶化量: ml) J	0.12	0.15	0.10	0.10	0.14	0.18	0.16

- Key: 1 Application Example  
 2 Dry cleaning detergent composition  
 3 Nonionic surfactant 1<sup>\*1</sup>  
 Nonionic surfactant 2<sup>\*2</sup>  
 Nonionic surfactant 3<sup>\*3</sup>  
 Nonionic surfactant 4<sup>\*4</sup>  
 Polyoxyethylene nonyl phenyl ether<sup>\*5</sup>  
 Polyoxyethylene alkyl ether  
 Lauric acid diethanolamide  
 Sorbitan monolaurate  
 Sulfosuccinic acid di-2-ethyl hexyl ester Na salt  
 Polyoxyethylene lauryl ether sesquiphosphoric acid esters<sup>\*5</sup>  
 Polyoxyethylene lauryl ether sulfuric acid ester-triethanol ammonium salt<sup>\*5</sup>  
 Stearyl dimethyl hydroxyethyl ammonium-para-toluene sulfonic acid salt  
 Stearyl dimethyl hydroxyethyl ammonium glycolic acid salt  
 Stearyl dimethyl ethyl ammonium monoethyl sulfuric acid salt  
 Triethanolamine  
 Water  
 Petroleum solvent<sup>\*7</sup>  
 pH (raw solution, 25°C)  
 4 Evaluation results  
 5 Washing ratio (%)  
 Recontamination ratio (%)  
 Hydrating performance

- 6 (State during mixing)  
(Water solubilization amount: mL)

[0032]

Table 2

		① 比較例				
		1	2	3	4	5
③ ドライ クリー ニン グ 用 洗 浄 剤 組 成 物	③ 非イオン界面活性剤1 <sup>*1</sup>					
	非イオン界面活性剤2 <sup>*2</sup>					
	非イオン界面活性剤3 <sup>*3</sup>					
	非イオン界面活性剤4 <sup>*4</sup>					
	ポリオキシエチレンノニルフェニルエーテル <sup>*5</sup>	43	38			
	ポリオキシエチレンアルキルエーテル <sup>*6</sup>			38	33	30
	ラウリン酸ジエタノールアミド				10	
	ソルビタンモノラウレート					10
	スルホコハク酸ジ-2-エチルヘキシルエステルNa		12	12	8	8
	ポリオキシエチレンラウリルエーテルセスキリン酸エステル <sup>*5</sup>				10	10
	ポリオキシエチレンラウリルエーテル硫酸エステル・トリエタノールアンモニウム <sup>*5</sup>					
	ステアリルジメチルヒドロキシエチルアンモニウム・パラトルエンスルホン酸塩					
	ステアリルジメチルヒドロキシエチルアンモニウム・グリコール酸塩					
	ステアリルジメチルエチルアンモニウム・モノエチル硫酸塩	7				
	トリエタノールアミン				3	3
④ 評 価 結 果	水		2		2	
	石油系溶剤 <sup>*7</sup>	50	48	50	34	39
	pH(原液, 25°C)	7.5	6.7	6.8	7.0	6.8
	⑤ 洗浄率(%)	52	50	36	42	40
	再汚染率(%)	12	13	19	16	15
	抱水性	(混合時の状態) ⑥	△	△	x	x
		(水可溶化量: ml)	0.05	0.05	0.01	0.01
			0.05	0.05	0.01	0.03

- Key: 1 Comparative Example  
 2 Dry cleaning detergent composition  
 3 Nonionic surfactant 1<sup>\*1</sup>  
 Nonionic surfactant 2<sup>\*2</sup>  
 Nonionic surfactant 3<sup>\*3</sup>  
 Nonionic surfactant 4<sup>\*4</sup>  
 Polyoxyethylene nonyl phenyl ether<sup>\*5</sup>  
 Polyoxyethylene alkyl ether  
 Lauric acid diethanolamide  
 Sorbitan monolaurate  
 Sulfosuccinic acid di-2-ethyl hexyl ester Na salt  
 Polyoxyethylene lauryl ether sesquiphosphoric acid esters<sup>\*5</sup>  
 Polyoxyethylene lauryl ether sulfuric acid ester triethanol ammonium salt<sup>\*5</sup>  
 Stearyl dimethyl hydroxyethyl ammonium-para-toluene sulfonic acid salt  
 Stearyl dimethyl hydroxyethyl ammonium glycolic acid salt  
 Stearyl dimethyl ethyl ammonium-monoethyl sulfuric acid salt  
 Triethanolamine  
 Water  
 Petroleum solvent<sup>\*7</sup>  
 pH (raw solution, 25°C)  
 4 Evaluation results

- 5      Washing ratio (%)  
         Recontamination ratio (%)  
         Hydrating performance
- 6      (State during mixing)  
         (Water solubilization amount: mL)

[0033]

#### Effect of the invention

The dry cleaning detergent composition of the present invention has excellent washing performance and recontamination-preventing capability as well as is excellent in the hydrating performance. Therefore, the dry cleaning detergent composition is appropriate as a washing agent for use in combination with a petroleum solvent in washing and as a sasara liquid for use in the pretreatment, in dry cleaning using a petroleum solvent as a washing medium, in particular.